

IMPACT OF FLUID-ROCK INTERACTIONS ON ENHANCED GEOTHERMAL SYSTEMS WITH CO₂ AS HEAT TRANSMISSION FLUID

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Abstract

There is growing interest in the novel concept of operating Enhanced Geothermal Systems (EGS) with CO₂ instead of water as heat transmission fluid (CO₂-EGS). Numerical simulations of fluid dynamics and heat transfer indicate that CO₂ may be superior to water in its ability to mine heat from hot fractured rock. Carbon dioxide also offers advantages with respect to wellbore hydraulics, in that its larger expansivity as compared to water would increase buoyancy forces and reduce the parasitic power consumption of the fluid circulation system. While the thermal and hydraulic aspects of a CO₂-EGS system look promising, major uncertainties remain with regard to chemical interactions between fluids and rocks. We have performed reactive transport modeling to study the impact of fluid-rock interactions on CO₂-EGS. Data from the quartz monzodiorite unit at the Desert Peak EGS site (Nevada) were used for the modeling analysis. A five-spot well configuration in a two-dimensional model was chosen to investigate (1) mineral alteration and associated porosity changes, and (2) impacts on reservoir growth and longevity, with ramifications for sustaining energy recovery, for estimating CO₂ loss rates, and for figuring tradeoffs between power generation and CO₂ mineralization (geologic storage).

Key words: Enhanced geothermal system, CO₂-EGS, Fluid-rock interaction, Heat transmission, Numerical modeling.

1. Introduction

With increasing concerns about carbon dioxide emissions into the atmosphere, Donald W. Brown (2000) proposed the new concept of operating Enhanced (or engineered) Geothermal Systems (EGS) with supercritical CO₂ instead of water as heat transmission fluid. Such a scheme could combine

recovery of geothermal energy with simultaneous geologic storage of CO₂. Compared with water, Brown noted that CO₂ has some favorable properties, including larger expansivity and lower viscosity, and is not a good solvent for rock minerals. He also pointed out unfavorable properties, such as lower specific heat of CO₂. In recent years, many studies have been undertaken to investigate various aspects relevant to CO₂-EGS systems, such as mechanical, CO₂-brine-rock reaction, and heat transmission, and CO₂ mineralization or sequestration (Liu et al., 2003; Rosenbauer et al., 2005; Ueda et al., 2005; Pruess, and Azaroual 2006; Pruess 2006, 2008; ; Xu et al., 2008; Spycher and Pruess, 2010). Advantages of EGS with CO₂ include increased heat extraction rates and wellbore flow compared to water-based systems and lesser potential for unfavorable rock-fluid chemical interactions (Pruess, 2006 and 2008). The solubility of CO₂ in water has implications for long term carbon sequestration and water-rock interactions (Liu et al. 2003; Rosenbauer et al. 2005; Xu et al. 2006 and 2008). The solubility of water into CO₂ is also important because it may affect the reaction of CO₂ with surrounding rocks and porosity and then permeability of rock (McGrail et al., 2009). The effects depend on the time required for removal of a free aqueous phase and the lithology of rock and engineered systems. Therefore, it is important to investigate geochemical processes and associated changes in porosity and permeability of a CO₂-EGS system.

As shown in Figure 1, a fully developed EGS with CO₂ would consist of three distinct zones (Fouillac et al., 2004; Ueda et al., 2005), (1) a central zone or “core” (Zone 1) in which all aqueous phase has been removed by dissolution into the flowing CO₂ stream, so that the reservoir fluid is a single supercritical CO₂ phase; (2) a surrounding intermediate zone (Zone 2), in which the reservoir fluid consists of a two-phase water-CO₂ mixture; and (3) an outer or peripheral zone (Zone 3), in which the reservoir fluid is a single aqueous phase with dissolved CO₂.

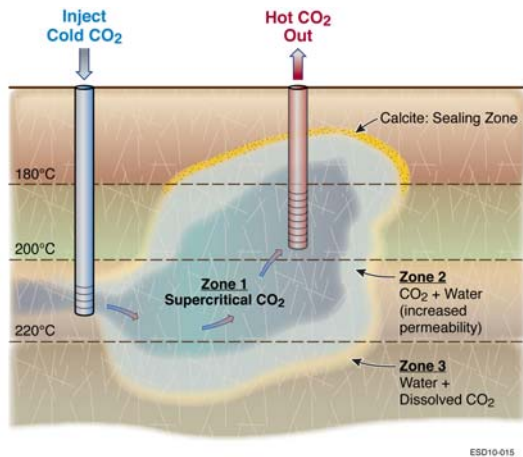


Figure 1. Schematic of the three zones created by injection of CO₂ into hot fractured rock (after Fouillac et al., 2004; Ueda et al., 2005).

Geochemical processes are expected to be quite different in the three zones. The absence of an aqueous phase in the inner (core) zone poses unique questions, as little is presently known about the geochemistry of non-aqueous systems. The aqueous fluids initially present in an EGS reservoir would be quickly removed by immiscible displacement by the CO₂, and by dissolution (evaporation) into the flowing CO₂ stream. Continuous operation of a CO₂-EGS may produce a rather dry CO₂ stream. Research on reactions between supercritical CO₂ and rocks in the absence of water has started only recently (Regnault et al., 2005; Jacquemet, 2006; McGrail et al., 2009). Carbon dioxide is not an ionic solvent, which would reduce the potential for dissolution and subsequent re-precipitation of minerals, and avoid problems of scaling and formation plugging (Brown, 2000). However, CO₂ can dissolve water, which can be chemically active (McGrail et al., 2009). It appears likely that prolonged exposure to supercritical (sc) CO₂ with small concentration of dissolved water will cause dehydration reactions that would remove loosely bound water from rock minerals. Such reactions may reduce the molar volume of the minerals involved, which would increase porosity and permeability of the formations, and might promote reservoir growth (Pruess and Azaroual, 2006). Anhydrous supercritical CO₂ could be quite reactive with some minerals. Regnault et al. (2005) performed lab experiments on batch reactions between pure minerals and sc CO₂ at 200°C and 105/160 bar. Portlandite (Ca(OH)₂) was totally carbonated to form calcite and aragonite; anorthite also displayed surface alteration patterns with secondary precipitation of fibrous calcite. The strong reactivity of portlandite suggests a potential for reactions with cement structures around the borehole, and a possible creation of short-cuts or increased

porosity. The properties of the cap-rock might be altered: due to its lower density, the sc CO₂ is bound to flow upwards to the cap-rock. Its lower viscosity might then enable it to migrate through the cap-rock; eventually, local reactions could occur, which could alter the sealing properties of the cap-rock.

Rock-fluid interactions in Zones 2 and 3 would be mediated by the aqueous phase. Some information on relevant processes is available from laboratory experiments (Liu et al., 2003; Ueda et al., 2005), natural CO₂-bearing geothermal systems (Wiese et al., 2006; Giolito et al., 2007), and reactive chemical transport modeling (André et al., 2007; Gherardi et al., 2007). Liu et al. (2003) conducted lab experiments using a batch micro-autoclave over a period of one week and a temperature range of 100-350°C to investigate granite and sandstone reactions in hot water in the presence or absence of excess CO₂. The experimental results showed that the dissolution of granite and sandstone and deposition of secondary minerals is enhanced by the addition of excess CO₂, particularly above 250°C. The major element concentrations of the residual fluids from the batch autoclave experiments were higher for the rock/H₂O/CO₂ system, but the sample weight loss was lower in the rock/H₂O/CO₂ system than in the CO₂ free system. Combined with the results of the collected gas volume and the presence of new calcium silicate phases, these findings suggest that dissolved CO₂ is fixed in the rock by the formation of secondary minerals. Ueda et al. (2005) performed experiments on CO₂-water-rock interaction at a temperature of 200°C to examine the possibility of CO₂ sequestration and fixation as carbonate minerals in geothermal fields, using granodiorite samples from the Ogachi hot/dry rock field. Their results suggest that injection of CO₂ into geothermal waters in granodiorite would promote Ca release from minerals such as plagioclase and anorthite, and precipitation of secondary carbonate minerals.

The peripheral zone (Zone 3) of an EGS operated with CO₂ may experience a combination of mineral dissolution and precipitation effects that could impact reservoir growth and longevity. The long-term behavior of this outermost zone will be crucial for sustaining energy recovery, for estimating CO₂ loss rates, and for figuring tradeoffs between power generation and geologic storage of CO₂. We have performed reactive geochemical transport simulations to study CO₂ induced mineral alteration in the outer zone, estimating associated changes in reservoir porosity, and sequestration of CO₂ by secondary carbonate precipitation.

Basic issues in CO₂-EGS systems include the physical and chemical changes induced by dissolved CO₂, including dissolution of primary minerals, formation of secondary minerals, CO₂ mineral

trapping, and changes in reservoir porosity and permeability. In the present study, thermal condition and mineralogical composition were taken from Well DP 23-1 of Desert Peak (Nevada) geothermal field (Xu et al., 2009), which is located within the Hot Springs Mountains approximately 50 miles (80 km) northeast of Reno, Nevada (Schochet et al., 2003). The potential reservoir under investigation is contained within pre-Tertiary metamorphic and granitic rocks with temperatures exceeding 204°C (Benoit et al., 1982; Lutz et al., 2004; Xu et al., 2009).

2 PROBLEM SETUP

2.1 Geometric and Flow Conditions

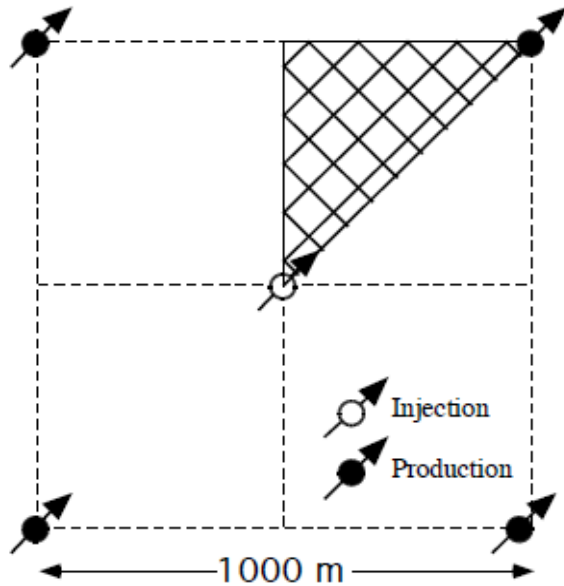


Figure 2. Five-Spot well pattern with computational grid for modeling a 1/8 symmetry domain.

We employed a five-spot pattern as used in Pruess (2008) for modeling heat transfer and fluid dynamics of a CO₂-EGS system (Fig. 2). The EGS reservoir was modeled as a fractured system with three orthogonal fracture sets at $D = 50$ m spacing. Matrix blocks were assumed impermeable, and the method of “multiple interacting continua” (MINC; Pruess and Narasimhan, 1985) was used to represent matrix-to-fracture heat transfer. The symmetry of the five-spot well pattern allows to limit the model to a 1/8 symmetry domain. All simulation results will be reported on a full-well basis. Reservoir thickness was assumed as 305 m, so that the reservoir volume per injector-producer pair was 0.3 km³. Fluid circulation was induced by specifying a certain pressure drop of typically 20 bar between the injection and production sides of the reservoir.

The process considered is injection of CO₂ into an initially water-saturated fractured reservoir at temperature and pressure conditions of $(T, P) = (210^\circ\text{C}, 200 \text{ bar})$. Injection temperature is 20°C with a pressure of 210 bar while fluid production occurs against a downhole pressure of 190 bar.

Table 1. Geometric and hydrogeologic specifications for the simulation

Formation	
thickness	305 m
fracture spacing	50 m
permeable volume fraction	2%
permeability	$50.0 \times 10^{-15} \text{ m}^2$
porosity in permeable domain*	50%
rock grain density	2650 kg/m ³
rock specific heat	1000 J/kg/°C
rock thermal conductivity	2.1 W/m/°C
Initial Conditions	
Reservoir fluid	all water
temperature	210 °C
pressure	200 bar
Production/Injection	
pattern area	1 km ²
injector-producer distance	707.1 m
injection temperature	20 °C
injection pressure (downhole)	210 bar
production pressure (downhole)	190 bar

2.2 Mineralogical Composition and Reaction Kinetics

The initial mineralogical composition used in the modeling is summarized in Table 2. The composition specified was based on the mineralogy of the crystalline rock of pre-Tertiary unit 2 (pT2) from well DP 23-1 of Desert Peak (Nevada) geothermal field, as previously used by Xu et al. (2009). Plagioclase was modeled using 50% low-albite and 50% anorthite. Other trace minerals including epidote, pyrite, and biotite were not considered in the model, because their reactions with the injected fluid are slow and not important for the chemical purpose. Details of the primary mineral composition can be found in Xu et al. (2009).

Dolomite, siderite, ankerite, dawsonite, smectite, and kaolinite could be formed after CO₂ injection and are specified as secondary minerals in the simulations. Almost all possibilities of secondary carbonate and clay minerals could be covered in our simulations, which are based on previous modeling studies (Xu et al., 2008 and 2010). Parameters for the kinetics of mineral reaction used in the model, such as specific reactive surface area and kinetic parameter k_{25} and E_a , were taken from Xu et al. (2009 and 2010).

The initial water chemistry is in equilibrium with the initial mineralogy at a reservoir temperature of 210°C. The resulting chemical compositions of the initial water can be found in Xu et al. (2009).

Table 2. Initial mineralogical compositions used in the numerical modeling.

Mineral:	Quartz monzodiorite (% in terms of solid)
Quartz	30
Calcite	1
Albite -Low	21.5
Anorthite	21.5
K- Feldspar	13
Chlorite	2
Illite	3
No-reactive	8

3. Simulation Tool

The present simulations employed the nonisothermal reactive transport code TOUGHREACT (Xu et al., 2006). This code introduces reactive chemistry into the multiphase fluid and heat flow code TOUGH2 (Pruess, 2004). A new fluid property module, ECO2H, based on Spycher and Pruess (2010) work was used. This module provides an accurate description of the thermophysical properties of mixtures of water and CO₂ under conditions typically encountered in CO₂-EGS systems of interest (12°C ≤ T ≤ 250°C; 1 bar < P ≤ 600 bar).

Temporal changes in reservoir rock porosity and permeability due to mineral dissolution and precipitation can modify fluid flow path characteristics. This feedback between flow and chemistry is considered in the code. Changes in porosity are calculated from variations in mineral volume fractions. Several porosity-permeability models are available, including a simple cubic Kozeny-Carman grain model as used in the present simulations. A broad range of subsurface thermal-physical-chemical processes are considered under various thermohydrological and geochemical conditions of pressure, temperature, water saturation, ionic strength, pH and Eh. Further details on the process capabilities of the TOUGHREACT code are given in Xu et al. (2006).

4. Results and discussion

Simulation results are given in Figs. 3-9. Initial fluid production in response to supercritical CO₂ (sc CO₂) injection is single-phase water (because the reservoir is initially water saturated). Breakthrough of sc CO₂ at the production well occurs after 44 days, and subsequently a two phase water-CO₂ mixture is produced (Fig. 3). Over time the rate of gas (mainly sc CO₂ and some vapor) saturations in the reservoir increase from the continuous sc CO₂ injection (Fig.

4). After 3.2 years, there is only gas phase in the produced fluid and this condition will last as long as CO₂ injection continues. At the time when aqueous phase ceases to be produced, the produced CO₂ includes approximately 7.1% by weight of dissolved water. The water content in the produced fluid declines fairly rapidly afterwards, due to partial reservoir dry-out in the fractures, dropping below 1% after 6.62 years, and below 0.1% after 15.6 years. Compared with simulation results in Pruess (2008), the results is very similar. We observe that water content (vapor) in produced gas will persist for a long time. The presence of dissolved water in the CO₂-rich phase may cause corrosive attack on reservoir rocks and well construction materials that require further investigation (McGrail et al., 2009).

Fig. 4 also shows temperature evolution over time in the grid block next to the production well. Due to heat depletion in the reservoir, temperature is gradually decreasing. Details on heat and fluid dynamics for this system are discussed in Pruess (2008).

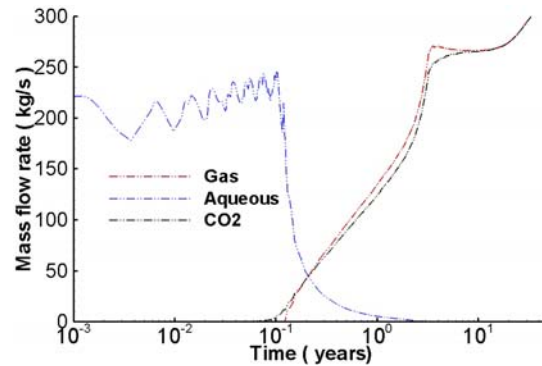


Figure 3. Simulated production behavior of EGS system in response to injection of supercritical CO₂ at constant downhole pressure of 210 bar (the location is the grid next to the production well).

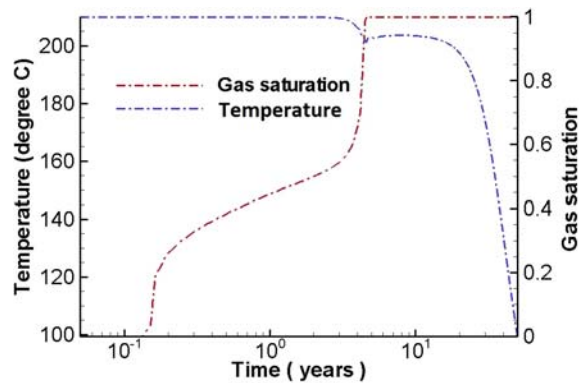
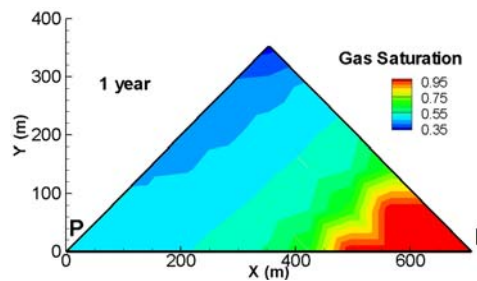


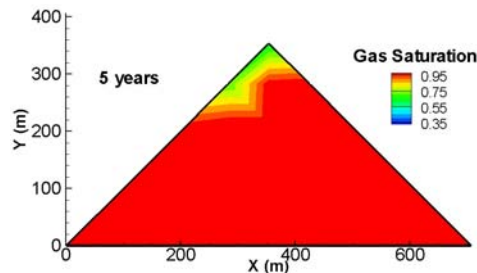
Figure 4. Temperature evolution over time at the grid next to the production well.

For an EGS, the behavior of the fracture system is of main interest, so we first analyze the chemical reactions in this domain. After 10 years the fracture domain (pore space) is mainly occupied by the gas phase (Fig. 5). It was assumed that no chemical reactions occur between the gas phase and rock minerals. Therefore, we discuss chemical interactions from the beginning until 10 years.

At the beginning of injection of supercritical CO₂, CO₂ dissolution into groundwater increases the total dissolved CO₂ concentration (Fig. 6) and lowers pH (Fig. 7). The lowered pH induces dissolution of primary minerals and precipitation of secondary mineral. Primary minerals such as K-feldspar (Fig. 8), chlorite (Fig. 9), anorthite, and albite dissolve. At the same time, secondary carbonate and clay minerals such as calcite (Fig. 10), siderite (Fig. 11), ankerite (Fig. 12), and smectite (Fig. 13) precipitate. Slightly more dissolution and precipitation occurs toward the production well along the main flow direction because water was removed gradually. The mineral reaction processes cause tiny decreases in porosity in the fracture domain (Fig. 14), then small changes in permeability. Total CO₂ sequestered by carbonate precipitation is presented in Figure 15. Close to the production well, a maximum amount of about 2 kg CO₂ was trapped in one m³ fracture medium.



(a) Gas saturation at 1 years



(b) Gas saturation at 5 years

Figure 5. Gas saturation profiles at different times obtained from the simulation (Injection well at $x=707.1$ m, projection well at $x=0$ m)

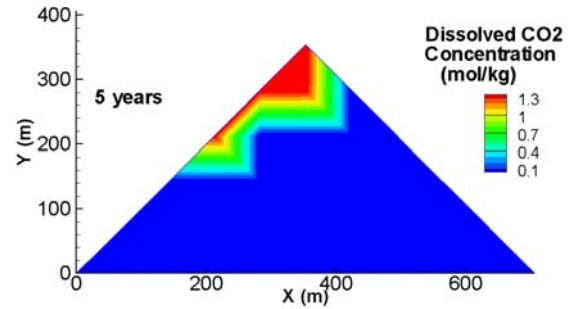


Figure 6. Total dissolved CO₂ Concentration after 10 years of injection.

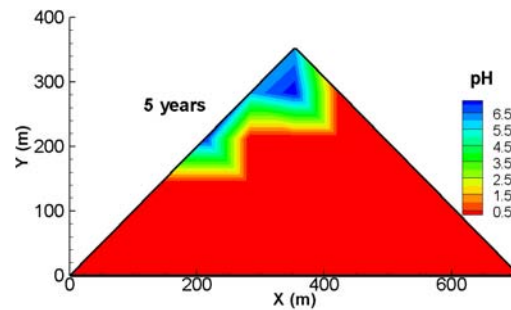


Figure 7. Distribution of pH after 5 years of injection.

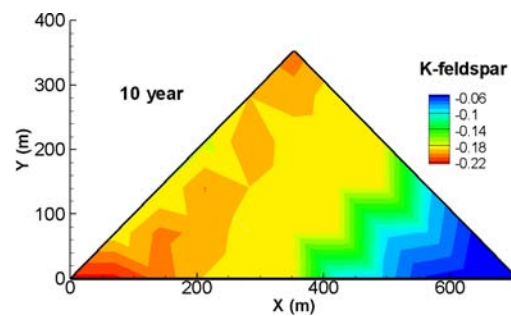


Figure 8. Change of *K_feldspar* volume fraction (in percentage) after 10 years (positive values indicate precipitation, negative values dissolution).

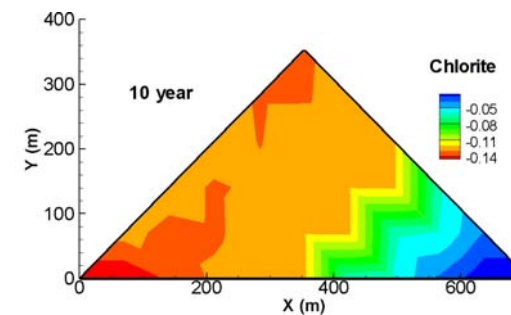


Figure 9. Change of chlorite volume fraction (in %) after 10 years.

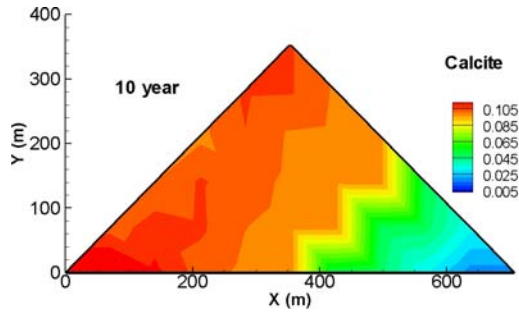


Figure 10. Change of calcite volume fraction (in %) after 10 years.

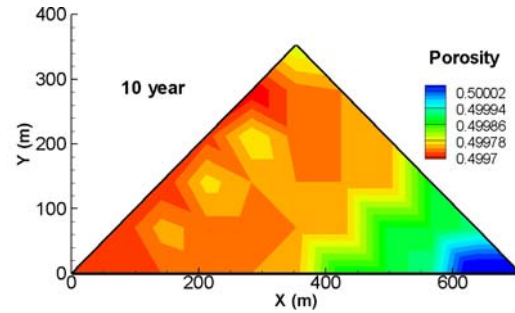


Figure 14. Distribution of porosity after 10 years.

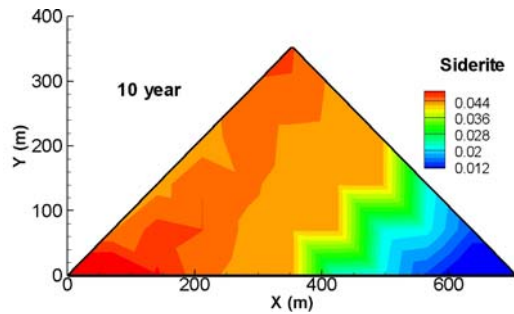


Figure 11. Change of siderite volume fraction (in %) after 10 years.

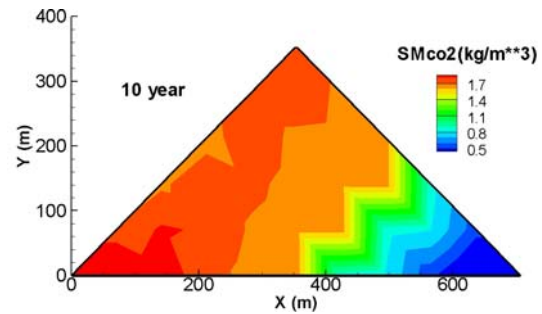


Figure 15. Cumulative CO₂ sequestered by carbonate mineral precipitation after 10 years.

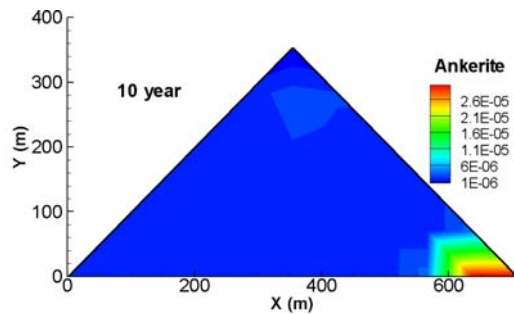


Figure 12. Change of ankerite volume fraction (in %) after 10 years.

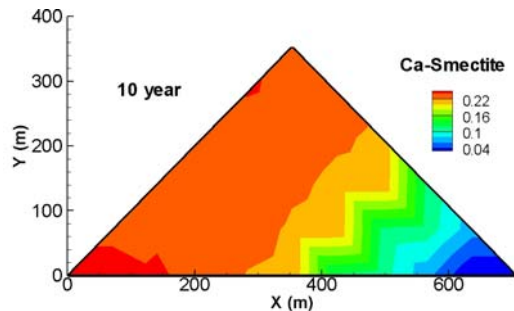


Figure 13. Change of Ca-smectite volume fraction (in %) after 10 years.

Now we select a grid block next to the production well ($x = 636.4$ m) to analyze the mineral alterations in the different matrix subdomains. Temperatures are increasing from the outside towards the inside of the matrix block (Fig. 16). Compared to the fracture, the gas phase invades the matrix much more slowly because of low permeability, then the gas saturation gradually increases, but remains under two-phase mixing condition for the simulation time (Fig. 17). Mineral-water reactions start at about five years (Figs. 18-22). The pattern of mineral dissolution and precipitation in the matrix is generally similar to the fracture domain, but the amounts are much larger than those in the fractures.

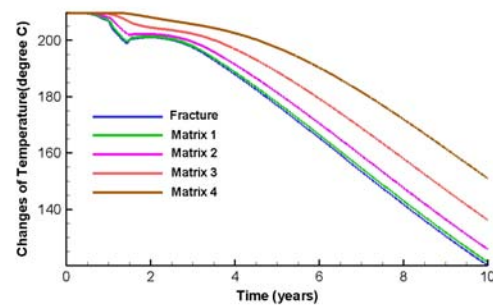


Figure 16. Changes of temperature over time for different subgrids of the fracture-matrix block. (Matrix 1, Matrix 2, Matrix 3, and Matrix 4 subgrids are ordered from the outside to inside).

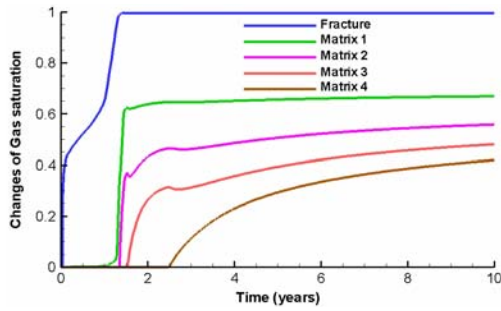


Figure 17. Changes of gas saturation over time for different subgrids of the fracture-matrix block.

The lowered pH and change in temperature cause mineral alternation, dissolution of K-feldspar and chlorite is presented here in Figs. 18 and 19. Compared to fracture, matrix subdomains have significant amounts of mineral dissolution. Mineral dissolution and availability of CO₂ from the aqueous phase result in precipitation of carbonate and clay minerals, and only calcite, siderite, smectite-Ca are presented here in Figs 20, 21, and 22. Similar to dissolution, the matrix has much more amounts of mineral precipitation.

Precipitation of carbonate minerals sequesters significant CO₂ in the matrix, with a maximum value of 18 kg/m³ medium (Fig. 23). Compared with fracture, matrix domain is main zone to storage CO₂. Precipitation of carbonate and clay minerals causes a substantial decrease in porosity in the matrix (Fig. 24). However, decreasing matrix porosity does not affect the main fluid flow in the fracture network system. The significant reactions in the matrix and precipitation of carbonate minerals are favorable for CO₂ mineralization (sequestration).

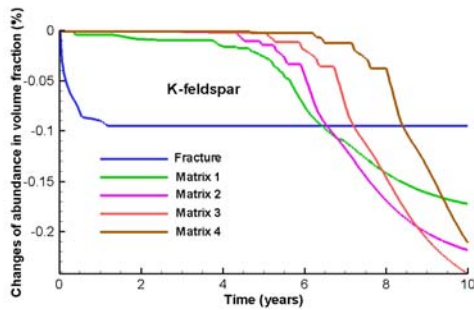


Figure 18. Changes of K_feldspar volume fraction over time for different subgrids of the fracture-matrix block.

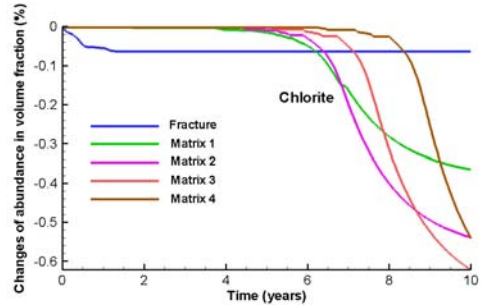


Figure 19. Changes of chlorite volume fraction over time for different subgrids.

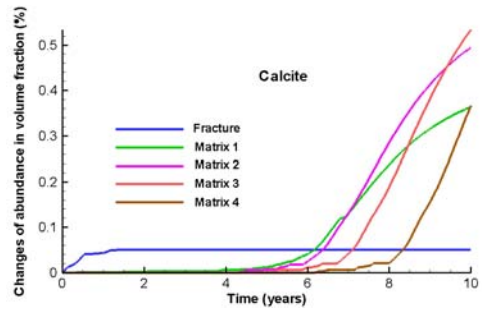


Figure 20. Changes of calcite volume fraction over time for different subgrids.

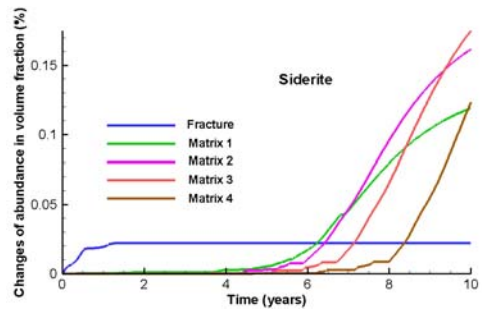


Figure 21. Changes of siderite volume fraction over time for different subgrids.

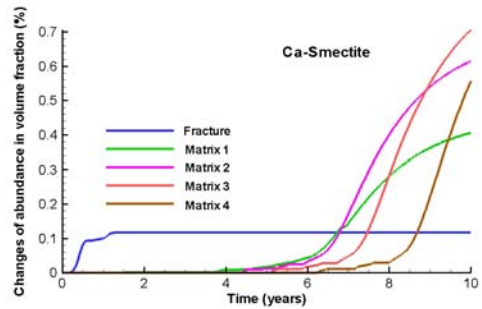


Figure 22. Changes of Ca-smectite volume fraction over time for different subgrids.

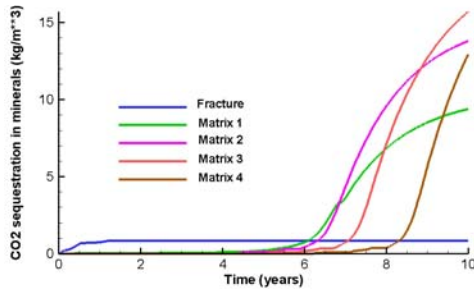


Figure 23. Cumulative CO₂ sequestered by carbonate mineral precipitation over time for different subgrids.

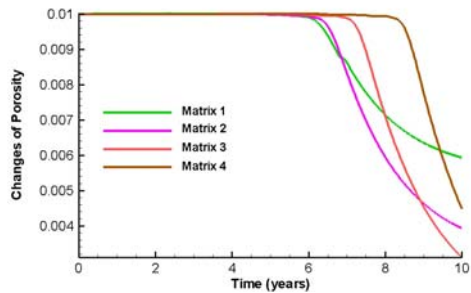


Figure 24. Porosity change profiles over time for different subgrids.

5. Conclusions

Reactive transport modeling for a five-spot well configuration of a possible CO₂-EGS has been performed using thermal condition and mineralogical composition of Desert Peak Well DP 23-1. Results indicate that a five-spot well pattern is suitable for a CO₂-EGS operation. The fracture domain of the system is quickly filled with injected supercritical CO₂. Aqueous phase based chemical reactions then stop, and no further mineral precipitation and porosity change occurs. On the other hand, the rock matrix remains in mixed two-phase CO₂-water conditions, and mineral alteration remains active for a long time. Precipitation of carbonate minerals traps significant CO₂ in the matrix, favorable for CO₂ storage. Therefore, using this pattern we can achieve both sustained geothermal energy recovery and CO₂ geologic storage.

We have only analyzed a 2-D flow regime. In fact, 3-D effects are expected to be important because the density of supercritical CO₂ is lower than water and buoyancy forces move CO₂ upward toward the caprock. In the future, we will examine 3-D effects on mineralization especially at the bottom of the reservoir. Future studies also include (1) using a range of different mineral compositions, (2) examining other injection-production well patterns,

and (3) evaluating dry CO₂ reactions with well construction materials and caprocks.

6. Acknowledgment

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References

- André, L., Audigane, P., Azaroual, M., Menjot, A. (2007), "Numerical modeling of fluid-rock chemical interactions at the supercritical CO₂ - liquid interface during CO₂ Injection into a carbonate reservoir, the Dogger Aquifer (Paris Basin, France)", *Energy Conversion Management*, **48**, 1782-1797.
- Brown, D. (2000), "A Hot Dry Rock geothermal energy concept utilizing supercritical CO₂ instead of water". Proceedings of the Twenty-Fifth Workshop on Geothermal Reservoir Engineering, Stanford University, 233-238.
- Benoit W.R., Hiner J.E., Forest R.T. (1982), "Discovery and geology of the Desert Peak Geothermal Field: A case history," Nevada Bureau of Mines and Geology Bulletin, **97**, 82.
- Fouillac, C., Sanjuan, B., Gentier, S. and Czernichowski-Lauriol, I. (2004), "Could Sequestration of CO₂ be Combined with the Development of Enhanced Geothermal Systems?", paper presented at Third Annual Conference on Carbon Capture and Sequestration, Alexandria, VA, May 3-6.
- Gherardi, F., Xu, T., Pruess, K. (2007), "Numerical modeling of self-limiting and self-enhancing caprock alteration induced by CO₂ storage in a depleted gas reservoir", *Chemical Geology*, **244**, 103-129.
- Giolito, Ch., Ruggieri, G., Gianelli, G. (2007), "Fluid evolution in the deep reservoir of the Mt. Amiata Geothermal Field, Italy", *Geothermal Resources Council Transactions*, **31**, 153-158.
- Jacquemet, N. (2006), "Durabilité des matériaux de puits pétroliers dans le cadre d'une séquestration géologique de dioxyde de carbone et d'hydrogène sulfuré", PhD Thesis, University Henri Poincaré, Nancy, France.

- Lutz S.J., Tait A.R., Morris C.L. (2004), "Stratigraphic relationships in mesozoic basement rocks at the Desert Peak east EGS area, Nevada," Proceedings of Twenty-Ninth Workshop on Geothermal Reservoir Engineering (ed. Horne R.N.), Stanford University, Stanford, California.
- Liu, L., Suto, Y., Bignall, G., Yamasaki, N., Hashida, T. (2003), "CO₂ injection to granite and sandstone in experimental rock/hot water systems", *Energy Conversion & Management*, **44**, 1399-1410.
- MIT. (2006), "The Future of Geothermal Energy Impact of Enhanced Geothermal Systems (EGS) on the United States in the 21st Century," A Report for the U.S. Department of Energy, Massachusetts Institute of Technology.
- McGrail, B.P., Schaefa, H.T., Glezakoub, V.A., Dangb, L.X., Owena, A.T. (2009), "Water Reactivity in the Liquid and Supercritical CO₂ Phase: Has Half the Story Been Neglected?" , *Energy Procedia*, **1**, 3415–3419.
- Pruess, K. (2006), "Enhanced Geothermal Systems (EGS) Using CO₂ as Working Fluid - A Novel Approach for Generating Renewable Energy With Simultaneous Sequestration of Carbon", *Geothermics*, **35**, 351-367.
- Pruess, K., Azaroual, M. (2006), "On the feasibility of using supercritical CO₂ as heat transmission fluid in an engineered hot dry rock geothermal system," In: Proceedings of the Thirty-First Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, USA, 386–393.
- Pruess, K. (2004), "The TOUGH Codes - A family of simulation tools for multiphase flow and transport processes in permeable media", *Vadose Zone Journal*, **3**, 738-746.
- Pruess, K. (2008), "On Production Behavior of Enhanced Geothermal Systems with CO₂ as Working Fluid", *Energy Conversion and Management*, **49**, 1446-1454.
- Regnault, O., Lagneau, V., Catalette, H., Schneider, H. (2005), "Étude Expérimentale de la Réactivité du CO₂ Supercritique vis-à-vis de Phases Minérales pures," Implications pour la Sequestration Géologique de CO₂. *C. R. Geoscience*, **337**, 1331–1339.
- Rosenbauer, R. J., Koksalan, T., Palandri, J. L. (2005), "Experimental investigation of CO₂-brine-rock interactions at elevated temperature and pressure: Implications for CO₂ sequestration in deep-saline aquifers", *Fuel Processing Technology*, **86**, 1581-1597.
- Schochet. (2003), "Injection testing for an Enhanced Geothermal Systems project at Desert Peak, Nevada. Transactions", *Geothermal Resources Council*, **27**, 885 – 891.
- Spycher, N., Pruess, K.. (2010), "A Phase-Partitioning Model for CO₂-Brine Mixtures at Elevated Temperatures and Pressures: Application to CO₂-Enhanced Geothermal Systems", *Transport Porous Media*, **82**, 173–196.
- Ueda, A., Kato, K., Ohsumi, T., Yajima, T., Ito, H., Kaieda, H., Meycalf, R., and Takase, H. (2005), Experimental studies of CO₂-rock interaction at elevated temperatures under hydrothermal conditions," *Geochem. J.*, **39**, 417–425.
- Wiese, F., Friðriksson, P., Ármannsson H. (2006) , "CO₂ fixation by calcite in high temperature geothermal systems in Iceland", Report Prepared for Hitaveita Suðurnesja, Orkuveita Reykjavíkur, Landsvirkjun, and Orkustofnun, Iceland.
- Xu, T., Sonnenthal, E.L., Spycher, N., and Pruess, K. (2006), "TOUGHREACT: A Simulation Program for Non-isothermal Multiphase Reactive Geochemical Transport in Variably Saturated Geologic Media," *Computers & Geosciences*, **32**, 145-165.
- Xu, T., Pruess, K., Apps, J. (2008), "Numerical studies of fluid-rock interactions in enhanced geothermal systems (EGS) with CO₂ as working fluid", In Proceedings, Thirty-third Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, **January**, 28-30.
- Xu, T., Rose, P., Fayer, S., Pruess, K. (2009), "On modeling of chemical stimulation of an enhanced geothermal system using a high pH solution with chelating agent", *Geofluids*, **9**, 167-177.
- Xu, T., Kharaka, Y.K., Doughty, C., Freifeld, B.M., Daley, T.M. (2010), "Reactive transport modeling to study changes in water chemistry induced by CO₂ injection at the Frio-1 brine pilot", *Chemical Geology*, **271**, 153-164.